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## EFFECT OF ALUMINUM HYDROSOL ADDITIVES AND AN ELECTROMAGNETIC FIELD ON THE STRUCTURE AND TECHNICAL PROPERTIES OF CLAYEY MINERALS

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The effect of nanosize hydrosols and organic xerogels of aluminum oxide on the properties of water suspensions modified by nanosols of bentonite and refractory clays is studied. The dependence of the properties of modified bentonite and refractory compositions on the type of nanosol and the effect of an electromagnetic field is studied according to the change in the increase and fluidity of the slip, the structure of the sol and the shrinkage and strength of fired samples.

**Key words:** nanodisperse particles, aluminum oxide hydrosol and organic aluminum sol, water suspensions of bentonite and refractory clay, structure of sols, properties of molding mixture and fired samples, electromagnetic field.

The present article analyzes the results of the latest research on the mechanism of the formation of an aluminum silicate complex when nanosols of aluminum and silicon oxides interact with natural silicates and aluminum silicates [1 – 3]. The technical parameters of mixtures and the properties of a material obtained on their basis can be changed in a desired direction by acting with Al and Si hydrosols on the exchange complex of clayey minerals and the quartz component of silicates without touching, which is especially important, the elemental makeup of the initial composition.

This research is based on the idea that the specific structure of a material starts to form at the intermolecular level where the systems are not in equilibrium and possess considerable internal energy, which promotes the evolution of structure [4, 5]. By activating at this level the initial structure of a material (adding modifiers, energy activation and others) it is possible to influence the process of formation of the final structure of the material. By studying at least some regularities in the formation of an aluminum silicate complex it is possible to learn how to model the technology of obtaining a wide class of materials, whose raw materials composition is based on silicates and aluminum silicates [4].

The main components of most molding mixes of aluminum silicate materials and casting molds used in metallurgy and elsewhere and responsible for the technical and strength characteristics of mixtures are refractory and bentonite clays.

The main minerals of these clays — kaolinite and montmorillonite — are two- and three-layer minerals consisting of silicon-oxygen octahedra, and the structural difference between these minerals are associated with the density of the crystal lattice and the distance between the regularly repeating groups of ions (planes) [6]. The greatest differences in the activity of the two minerals are attributed to the coordination of the aluminum ion in the structure: in the sixth coordination in kaolinite and in the sixth and fourth coordination in montmorillonite, which is thermodynamically unstable and chemically active in montmorillonites in the natural state and in kaolinite after dewatering (thermal activation). The removal of the most of the water from the three-layer minerals of montmorillonites gives rise to weaker amorphization than in two-layer minerals of the kaolin group because of the small amount of structural hydroxides [6]. For these reasons the clay-forming minerals are found in the metastable crystalline state. In this state the crystal lattice can change under the action of different factors: the interaction with aluminum sols containing aluminum [7, 8], electromagnetic activation [9, 10], thermal activation and others.

According to a principle of I. R. Prigogine, Nobel Laureate in Chemistry, nonequilibrium can serve as a source of ordering, which explains a general property of self-organization in open systems [11]. In other words self-organizing structures form far from equilibrium. By stimulating these processes it is possible to model the processes required for the production of improved materials.

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TABLE 1. Composition of the Experimental Clays

Clay	Content, wt. %						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O + Na <sub>2</sub> O
Nurlatskoe	56.4	20.0	1.13	7.00	1.61	2.78	2.0
Nizhneuvél'skoe	53.6	27.9	0.21	2.23	0.34	0.64	0.8

The wide assortment of natural aluminum silicates is explained by the strong specific interaction between the aluminum and silicon oxides, which occurs due to the similarity of the electronic properties of Al and Si. Since it is geometrically similar to Si(OH)<sub>4</sub> the aluminate ion Al(OH)<sub>4</sub><sup>-1</sup> can be introduced on the surface of SiO<sub>2</sub> or it can enter into exchange on it, thereby forming aluminum silicate sections with fixed negative charges [7]. The ends of the outer layers of the silicon oxide tetrahedra of an aluminum silicate packet of montmorillonite clays consist of O<sup>2-</sup>, which gives a comparatively weak bond between the layers [6]. Owing to this the crystal lattice of montmorillonite is mobile and tends to swell. For these reasons montmorillonite and bentonite clays absorb large quantities of water, do not easily give up water on drying and are very plastic and prone toward cracking. All this complicates the technology of using clays and requires the introduction of corrective fillers, such as quartz sands and surfactants, which adversely affects the process indices during heating. The crystal lattice of kaolinite is characterized by a relatively dense structure with the shortest distance between the packets owing to the presence of the anions (OH)<sup>-</sup> at one end of a packet and the cations H<sup>+</sup> at the other end and it is immobile and easily gives up water. Kaolinite of refractory clays swells much less in water and gives up the attached water comparatively easily on drying.

The instability of the rheological properties and the problems arising during molding are associated with the disordering of the crystal structure of the clay raw material. The properties are stabilized by means of different activation processes, among which the efficacy of hydrothermal treatment and the use of highly concentrated ceramic binding suspensions have been checked [4]. Electromagnetic methods of activation in ceramic technology are of interest because of the interlayer electrostatic charge of aluminum silicates.

Previous research [3] showed that aluminum sol (AZ-1) and especially organic aluminum sols (AZ-UK) actively affect some technical properties of silicates. It was observed that the organic component has a positive effect, which was explained by a possible interaction (co-polymerization) of the organic and inorganic (silica) components.

On this basis and previous investigations [3] it was important to check the action of aluminum sol (AZ-1) and organic aluminum sol (AZ-UK) on some technical properties of water suspensions of bentonite and refractory clays.

The action of hydrosols of silicon and aluminum oxides on, first and foremost, the silicate-containing components of

the molding mixture for crystalline and amorphous structures (sand, glass, loam) as well as bentonite clays, where the interlayer space is also associated with SiO<sub>2</sub> tetrahedra, was examined in previous articles. The research was based on the premises that the activity of clayey minerals is associated with the aluminum ion, its fourth and thermodynamically unstable coordination, which in montmorillonite is observed in the natural state and in kaolinite only after dewatering [6].

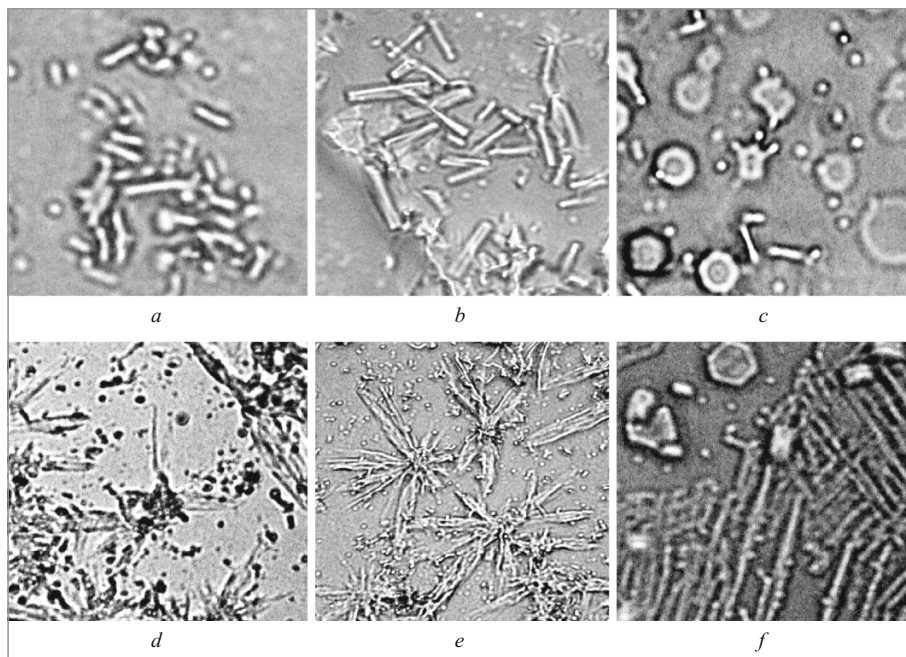
In addition, since the interpacket space of the main aluminum-silicate minerals is polar and lies in the range 0.72 – 2.14 nm and the particles of aluminum and silicon sols are polar, 4 – 9 nm in size, and active, it can be supposed that they are capable of displacing the H<sub>2</sub>O molecules from the intersheet space and occupy positions in the structural sequence during the formation of the aluminum silicate complex. This process should be reflected in a change in the technical properties of water suspensions of clays and will affect the properties of the materials. The previous works are devoted to these questions.

The strengthening (reinforcing) effect of colloidal silica on organic polymers [7] and the heightened chemical activity of amorphous (pseudoboehmite) aluminum oxide [8] are well known. In [9], in the course of research on the effect of an organic modifier on the silicate system it was shown that the strength increases and the water-absorption of the material decreases. The authors explained the observed effect by adsorption of an organic polymer on the walls of the pores and filler particles as well as by the partial interaction (co-polymerization) of the organic (polyester) and inorganic (silica) components of the binder in the contact zone. In addition, a film of the products of polymerization of the organic component forms on the extended surface of silicic acid xerogel, which makes the entire system more elastic.

The presence (in a material's microstructure) of a large quantity of such polymer films increases the resistance to destructive actions and, correspondingly, results in greater strength. The adsorption of an organic modifier on seed crystals blocks the subsequent growth of the seeds and the entire composition becomes stronger as dispersity increases [9].

In the present work bentonite clay from the Nurlatskoe deposit and Nizhneuvél'skoe refractory clay were used for further study of the mechanism leading to the formation of an aluminum-silicate complex (Table 1).

Hydro aluminum sol (AZ-1) with the boehmite crystallite-type structure with 3.5 – 4 nm particles and pH = 4 and acetic acid stabilized aluminum hydrosol (organic aluminum sol) AZ-UK, which comprised a viscous gel-like mass, from



**Fig. 1.** Microstructure of sols — 10 wt.% water suspensions ( $\times 1000$ ; reflected light): *a*) bentonite clay; *b*) bentonite clay with 0.1% AZ-1 addition; *c*) bentonite clay with 0.1% AZ-UK added; *d*) refractory clay; *e*) refractory clay with 0.1% AZ-1 added; *f*) refractory clay with 0.1% AZ-UK added.

$\text{AlCl}_3$  wastes were used as nanodisperse modifiers. The nanosols were synthesized at KazkhimNII, JSC.

The effect of aluminum sol (AZ-1) and organic aluminum sol (AZ-UK) on some technical properties of water suspensions was studied.

Ten-percent (by weight) water suspensions were prepared on the basis of the components chosen and distilled water. The base composition was a clay suspension; suspensions with additions of 0.1% (above 100%) AZ-1 and AZ-UK nanosols were used for comparison. The values of the parameters were recorded after the suspensions were kept for 24 h in 100-mm glass cylinders: presence of sol and precipitate and growth (swelling).

Thirty-six percent slips were prepared for molding. The fluidity of the slips was checked using suspensions prepared using different methods for mixing the components: 1) a mechanical mixer for 30 min and 2) a 20-watt MM-5 magnetic mixer for 30 min. The fluidity of the slip was recorded.

Samples of size  $50 \times 50 \times 50$  mm were molded from the slips. Some samples were dried to 5% moisture content at  $100^\circ\text{C}$ ; all others were fired at  $1000^\circ\text{C}$ . The volumetric shrinkage was recorded and compression tests were performed.

The shrinkage and strength of the samples were determined after drying and firing.

The microstructures of the sol samples after mechanically mixed water suspensions of clays modified by aluminum sols were allowed to cure for 1 day are shown in Fig. 1. Differences are evident in the fine structures of the clayey suspensions. Identical formations are observed for suspensions of pure clay and clay modified by AZ-1; these formations are larger ( $10 - 20\ \mu\text{m}$  in size) in the presence of AZ-1 than in the case of pure clay ( $5 - 10\ \mu\text{m}$ ). It is evident that

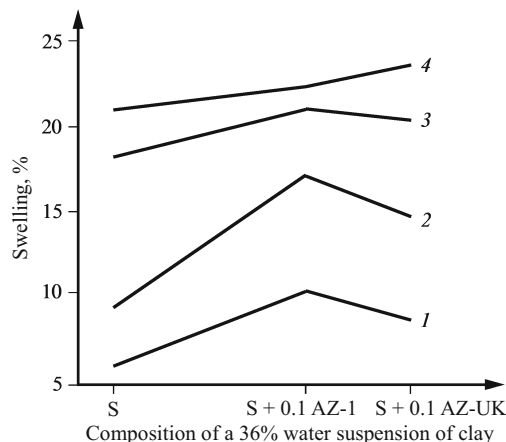
there is a difference between bentonite clay and refractory clay sol particles. The formation of  $5 - 15\ \mu\text{m}$  spherical particles was observed with modification of a suspension of AZ-UK bentonite clay. The picture is different from that observed for the refractory clay, for which a mesh (fibrous) structure is formed.

These differences should be reflected in the properties of slips. The spheres in bentonite clay can be explained by the formation of silica (or aluminum silicate) granules with a surface film consisting of an organic component, which correlates with partial interaction (co-polymerization) of organic and inorganic components in the contact zone. This increases the elasticity of the entire system [5, 6], in the present case a clay suspension based on bentonite clay, and changes the technical characteristics of slip toward greater growth (determined according to the increase in volume of the slip as a result of a change in the volume of the clay-containing minerals) (Fig. 2) and fluidity (Fig. 3). The opposite effect is observed for a suspension of refractory clay, which is also in agreement with the shape of the sol particles.

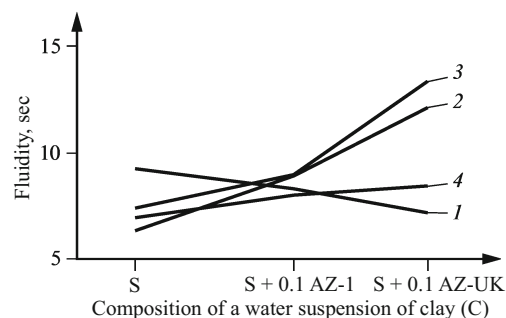
The dependence of the swelling of clays on the action of the modifier and the mixing method is shown in Fig. 2. An increase in swelling is observed for both clays, but especially for refractory clay; the introduction of aluminum sols has an even larger effect.

The preparation of clay suspensions in a magnetic mixer was reflected in the fluidity of the slips (see Fig. 3). The opposite effect is observed: fluidity decreases with the addition of aluminum sols, especially AZ-UK.

The test results for fired samples are presented in Fig. 4. Analysis of the graphical dependences shows that the addition of aluminum sols to a suspension of clays, especially AZ-UK, increases the shrinkage and strength of the samples.

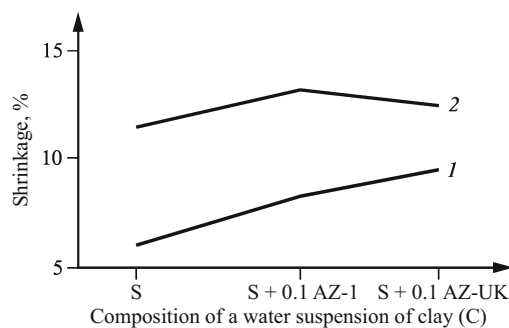


**Fig. 2.** Swelling of clays in water suspensions due to additions of nanosols — 0.1% AZ-1 and 0.1% AZ-UK: 1) suspension of refractory clay, mechanical mixing; 2) suspension of refractory clay, electromagnetic mixing; 3) suspension of bentonite clay, mechanical mixing; 4) suspension of bentonite clay, electromagnetic mixing.

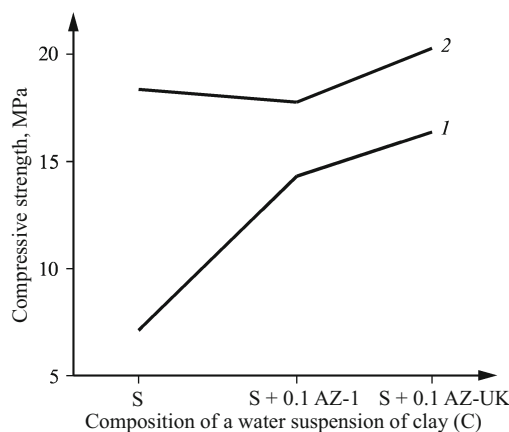


**Fig. 3.** Thinning of clay suspensions versus the addition of nanosols: 0.1% AZ-1 and 0.1% AZ-UK: 1) 36% water suspensions of bentonite clay, mechanical mixing; 2) 36% water suspensions of bentonite clay, electromagnetic mixing; 3) 36% suspensions of refractory clay, mechanical mixing; 4) 36% suspensions of refractory clay, electromagnetic mixing.

The electromagnetic action decreases the shrinkage for all pastes while the strength increases, which is especially important. The swelling and fluidity and the change in strength taken together make it possible to explain a previous supposition that the intersheet water of minerals is replaced by aluminum sols together with the electrostatics of the sheets changing. This makes it possible for an aluminum silicate complex to form in the intersheet space of the mineral and stabilizes the structure at the final stage, which manifests as an increase of the shrinkage and strength of fired samples. Since the strength of aluminum silicates is related mainly with the formation of mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) during firing, the addition of aluminum sol can promote this process. The effect due to the introduction of AZ-UK is identical to the results obtained in [3, 9] on the use of organic polymers and their role in the formation of the structure of aluminum silicates.



**Fig. 4.** Shrinkage (a) and strength in compression (b) of samples cast from mechanically mixed slips of 36% water suspensions of clays and fired at 1000 °C: 1) refractory clay; 2) bentonite clay.



**Fig. 5.** Strength in compression of samples cast from mechanically mixed slips of 36% water suspensions of clays and fired at 1000 °C: 1) refractory clay; 2) bentonite clay.

The present investigations have shown that in preparing clay suspensions the requisite technical properties of slip can be obtained and ultimately the strength of fired articles increased by combining the use of aluminum sols and an electromagnetic field.

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